A NOVEL INVESTIGATION ON BIOTIC AND ABIOTIC MOLECULES IN AN ICE MATRIX UNDER ENERGETIC CONDITIONS

Final Report

JPL Task 978

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A. OBJECTIVES

The objective of this one-year proposal was to demonstrate the scientific utility of an experiment which will allow for a better understanding of the chemical makeup of the ice-covered surfaces of planetary bodies. This includes at least part of the surface of each satellite of the gas giants, with a primary focus on surface conditions approximating Europa. Since no experimental set up would be able to simulate the actual conditions entirely (i.e. high-radiation environment by energetic particles such as electrons, photons, and ions; chemical composition, etc.) which are present on the surfaces of these bodies, especially on Europa, we proposed to perform a series of simple experiments to better understand the chemical processes taking place on these surfaces in such intense radiation environments. The objective was to freeze different amino acids at various temperatures (10K and 90K) in an H_2O ice matrix and perform spectroscopic measurements (i.e. reflectance measurements) before and after we bombard the ice surface with energetic particles. The concentrations (~1 organic molecule for 10,000 H_2O molecules), which are probably several orders of magnitude higher than one would expect to find on planetary surfaces, should result in very little amino acid-amino acid interactions. At the same time, they are expected to yield enough intensities to be identified spectroscopically.

Two different spectroscopic methods, Laser Raman and UV/VIS reflectance spectroscopy, were planned to be utilized to monitor the alteration of organic molecules so that complete spectral coverage could be obtained. Laser Raman was chosen because of its known utility in several applications and because it has been identified as a prime candidate for the 2009 Mars Science Laboratory (MLS) mission. UV/VIS reflectance spectroscopy (in the 110 nm to 700 nm wavelength range) was chosen because of its inclusion as part of most current and future missions. Finally, the lifetimes of the amino acids were planned to be determined by calculating the incident influx of radiation on the sample, and comparing the altered and unaltered material over various time intervals.

B. PROGRESS AND RESULTS

As mentioned earlier, the experiment was designed to perform two different types of spectroscopic measurements: 1) UV/VIS/NIR and 2) laser Raman spectroscopy. Because this was a brand-new experimental setup, it required several months to design, purchase parts and then construct.

1) UV/VIS/NIR Experiments: We had obtained funding through the JPL EIC to purchase a monochromator and a CCD detector system. An Acton 0.39 meter, triple grating, UV/VIS monochromator was purchased because of its ability to cover three wavelength ranges without breaking the vacuum. The Princeton Instruments CCD detector system was also purchased upon recommendation by an Acton design engineer to be used in conjunction with the monochromator. However, the CCD camera never worked correctly due to a faulty amplifier in the cryogenic part of the unit, and was sent to Princeton Instruments for repair. When the CCD was returned to us, we discovered that the CCD surface had become damaged in shipment, and thus the camera had to be returned to Princeton Instruments once again. This entire process came to a merciful conclusion in September of 2002, and the experiment instrumentation was finally in place. We have already completed the calibration process using a Hg vapor lamp (see Fig. 1). We are currently conducting experiments concerning the chemical evolution of the biotic and abiotic molecules in an ice matrix under energetic conditions, as was described in the original proposal

2) Laser Raman Experiments: While the UV/VIS apparatus was being constructed, we continued experiments on rock samples containing various amino acids with the portable laser Raman spectrometer (LRS) on loan to us from the University of Alabama at Birmingham. Fig 2 shows a spectrum of Phenylalanine as a single crystal taken with the LRS. One characteristic of the spectrometer was that while the wavelength of the features of phenylalanine crystal did not change, the relative intensities of them were dependent on the incident angle of the excitation laser. This was not expected, and caused concern for the ability of Raman to determine the quantitative amount of altered vs. unaltered material in the H_2O matrix during an experimental run. We obtained spectra of several other amino acids we had identified for use in the experiment, and the same effect was always observed.

To determine the effects of incident angle on mineralogy of samples, we obtained several dozen rock samples and attempted to determine the spectral properties of these samples. One of our objectives was to determine if there was functional dependence on incident angle when applied to rock samples. Figures 3 and 4 shows the Raman spectra of six of these samples. All the spectra were taken with 10 mW laser power and 10 sec scans. As expected, the spectra shows features clearly identifying the various rock samples. Furthermore, the relative intensities of these features were found to be independent of incident laser angle or specific spot location. To determine the ability to identify small concentrations of material, we attempted to do some Martian analog material (partially in conjunction with a Mars SCOUT proposal on which we were listed as Co-I's). We could unambiguously identify both crushed calcite and dolomite minerals when they were mixed with palagonite at the 10% level. Furthermore, we were able to identify calcite and dolomite in a mixture (Fig 5.)

Because we were getting outstanding mineralogical data from the LRS, we attempted to identify amino acids frozen in an H_2O matrix. Much to our surprise, no matter how we arranged the frozen mixture we never were able to obtain spectra of the amino acids. These attempts included a few % of both alanine and phenylalanine in both liquid and water ice. This was most likely due to the nature of H_2O and the incident laser wavelength. For example, in rock samples the incident radiation and the Raman excitation light come from the same spot on the surface, due to the opacity of the material. Therefore, focusing of the scattered Raman signal is not a problem. In water ice this is not the case, primarily due to the transparency of the material. Both the incident and excitation light can penetrate the sample, making detection of the Raman signal (which is on the order of 10^{-9} times less intense than the excitation signal) impossible.

C. SIGNIFICANCE OF RESULTS

The results of the LRS study are quite profound in terms of future use as an *in-situ* explorer. With minimal sample preparation, a small LRS can identify mineralogy in a very short time interval (usually less than a minute). This can happen even on different crushed minerals in a sand-type mixture if point counting is used. However, the identification of individual amino acids, especially in an ice matrix of some sort, is impossible. This has implications for an astrobiology-focused mission. If Raman spectroscopy is to be done for the goal of caching samples for later return to earth, the identification of Anthracite coal (See fig 4) with both graphitic and disordered carbon features might be all that is necessary to identify interesting samples (Schopf et al. 2001). However, individual organic components of a sample would need quite a bit of sample preparation before any data could be obtained from a sample. This would include doing surfaced enhanced Raman spectroscopy (SER), or pre-separation of material prior to identification.

Our experimental results regarding LRS measurements also resulted in our involvement in a $350 million JPL Mars SCOUT proposal which was recently submitted to NASA, A DRDF proposal submitted for FY03 funding, and a ASTEP proposal which will be submitted in May of 2003.

D. FINANCIAL STATUS

The total funding for this task was $145,000, all of which has been expended.

E. OTHER PERSONNEL

Dr. Luther Beegle (3264)
Dr. Sandor Trajmar (3264; on-call)
Prof. Thomas J. Wdowiak (UAB)
Prof. David Agresti (UAB
Prof. Perry Gerikines (UAB)
Dr. Charles Terrell (3264)
Dr. Yuk Yung (Caltech)

F. PUBLICATIONS AND PRESENTATIONS

[1] L.W. Beegle, I. Kanik and T. J. Wdowiak, “Laser Raman Spectroscopy of Mineralogical Samples From an Astrobiological Perspective,” to be presented at the 34th Annual Lunar and Planetary Science Conference, Houston TX, March 2003.

G. REFERENCES

[1] J.W. Schopf, et al., *Nature* **416** 73, 2002

H. APPENDIX: FIGURES

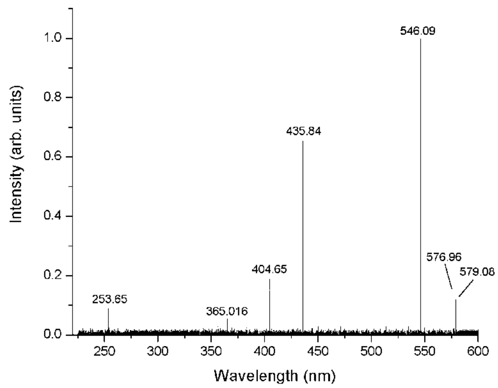

Fig. 1 Mercury lamp spectrum taken through one of the glass-windowed ports on the Ice Experiment chamber. Spectrometer slit width = 25 µm, 1200 gr/mm gratings, CCD exposure time = 0.1 s, CCD temperature = -20 ºC. Spectrum was normalized to the peak at 546.09 nm.

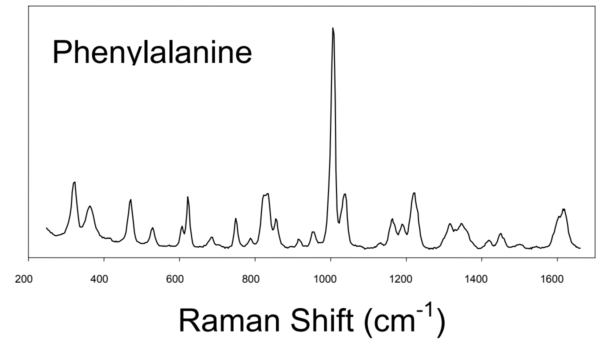

Fig 2 Phenylalanine take with the portable LRS. 10 mW laser operating power and a 10 sec. scan time.

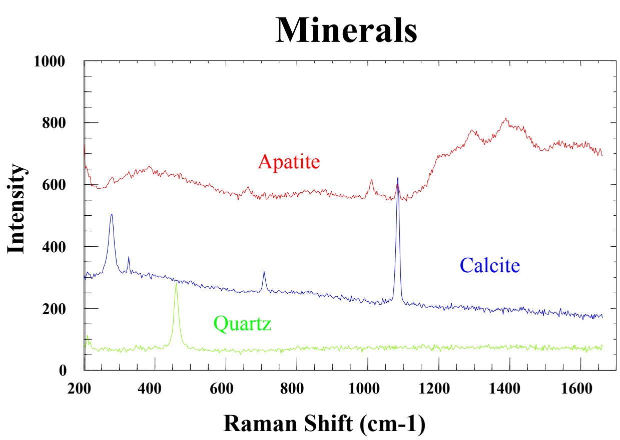

Fig 3 Laser Raman Spectra of three minerals, Apatite, Calcite and Quartz. Each spectra took 10 seconds of scan time on an unprepared surface.

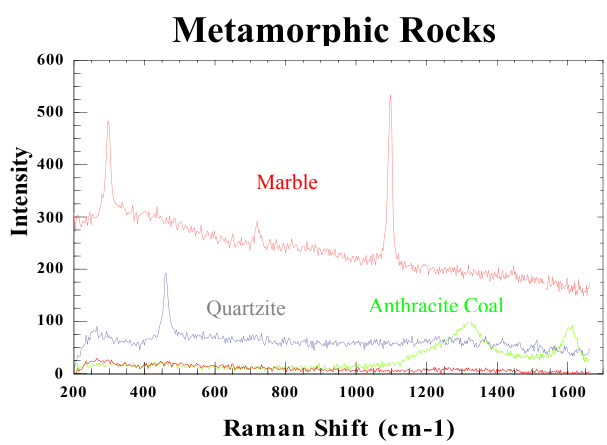

Fig 4 Laser Raman Spectra of three metamorphic rocks, Marble, Quartzite and Anthracite coal. Each spectra took 10 seconds of scan time on an unprepared surface.

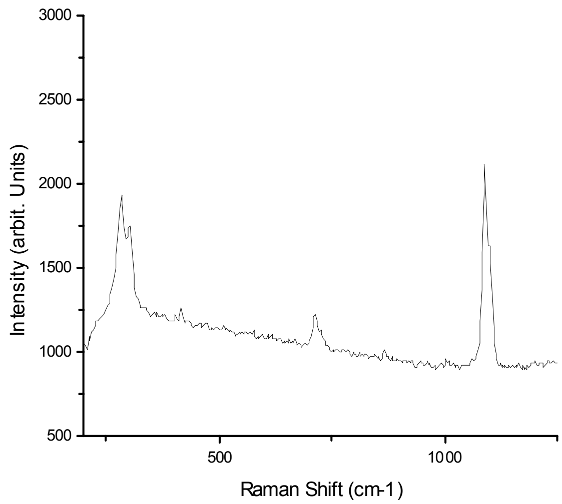

Fig 5 A laser Raman Spectra of a mixture of Calcite and Dolomite. The two minerals have a clearly distinguishable feature located at ~300 cm^{-1}.